A DIELECTRIC SLIT DIE FOR IN-LINE MONITORING OF POLYMER COMPOUNDING

Anthony J. Bur, National Institute of Standards and Technology, Gaithersburg MD 20899-8542
Michael McBrearty, Chemical ElectroPhysics Corp., Hockessin DE 19707

Abstract

The dielectric slit die is a new in-line instrument that is designed as a multipurpose sensing device to measure dielectric, rheological, and optical properties during extrusion. The instrument is mounted at the exit of an extruder and consists of a slit with dimensions 2 mm high by 28 mm wide by 15 cm length along which are situated dielectric, pressure and optical sensors. A flexible design permits interchanging of sensor locations and the addition of new sensors.

Introduction

In previous work we described a first generation dielectric sensor that we used for in-line monitoring of resin compounding.[1,2] That sensor consists of a ceramic ring that has interdigitating electrodes deposited on its inside surface. As an extruded resin flows through the ring, its dielectric properties are monitored by a fringing electric field that extends into the resin melt. Using this sensor, we reported the results of compounding resins with inorganic fillers and resin/nanoclay composites. We observed that dielectric properties are significantly impacted by filler content and microstructure.[3]

The interdigitating electrode design has the advantage that the sensor is one-sided and does not involve sensing across the full dimension of the flow stream. On the other hand, the interdigitating design has the disadvantage that the sensing electric field is confined to the near surface region. For a 12.7 mm diameter ring with interdigitating electrodes that are separated by 0.33 mm, the field extends only 0.4 mm into the resin melt. Consequently, only 10 % of the cross section of resin flow stream, a thin shell near the surface, is monitored. This is because the strength of the electric field decays from the surface with a characteristic decay length of d/3 where d is the interelectrode separation.[4] The electric field decay function for a 12.7 mm diameter ring having interelectrode separation of 0.33 mm is shown in Figure 1 where a sensitivity function is plotted versus distance from the surface. These data were obtained by inserting PMMA rods (polymethyl methacrylate) with a range of diameters into the sensor and measuring the response.[2] In the limit of zero gap between the PMMA and the electrode surface, the sensor must yield the relative permittivity of PMMA, which is 3.276 at room temperature and for applied voltage at 500 Hz.

Given that 90 % of the flow steam escapes examination with the ring design, we sought to develop a new sensor that has a slit configuration. The slit channel, with approximate dimensions of 2 mm high by 2.8 cm wide by 15 cm long, defines a constant geometry sample cell in which the processed material is characterized by on-line sensing devices. The primary sensor in the channel is the dielectric sensor consisting of interdigitated electrodes that are deposited and fired onto a ceramic substrate that forms one surface of the slit. Other sensors in the current design are pressure and optical sensors situated along the axial dimension of the slit. By keeping the slit height at 2 mm or less, it is possible to fix the interelectrode separation so that the fringing electric field extends significantly into the flow stream interrogating up to 50 % or more of the resin flow. The slit die has a flexible design that permits the addition of new sensors or instrumentation ports, or permits the interchange of sensors to different positions in the slit channel.

In this paper we will describe the sensor design and its capabilities as an on-line, real-time sensor. In a companion paper at this meeting, we present results of real-time monitoring of nanocomposites compounding.[5]

Sensor Design

Figure 2 is a schematic of the sensor as viewed from the side and front. Two semicircular stainless steel pieces, top and bottom halves, form the cylindrical geometry of the sensor. Its overall dimensions are 12.7 cm diameter by 15.24 cm long (5 inches diameter by 6 inches long), but the cell can be fabricated with a longer length for the purpose of adding additional instrumentation ports. Or, an additional port sector can be added in the sensor train. The sensor housing contains threaded instrumentation ports of the standard half-inch by 20 threads per inch type in addition to two cut out chambers for ceramic in-lays that are used for dielectric sensing. The ceramic piece on the bottom is high purity alumina onto which platinum electrodes have been deposited in an interdigatating pattern. The ceramic on top is made from machinable ceramic, has a trapezoidal cross section, and contains a cutout of the slit that is 2 mm deep by 2.8 cm wide extending over the length of the piece, approximately 11 cm. The depth and width dimensions of the slit were machined with an accuracy of 0.012 mm. The trapezoidal cross section serves to hold the piece into place in the top half stainless steel. A heating jacket surrounds the sensor and temperature is controlled using a thermocouple inserted into the body of the steel housing. A customized interface adapter plate positioned between sensor and extruder establishes the connection to the extruder. This plate

contains the appropriate threaded screw holes for the specific extruder being used.

Optional sensor port sectors, shown in Figure 3, can be added in-line, sandwiched between the slit die and the interface plate. Ancillary sensors such as UV or infrared absorption, optical microscope, ultrasonic velocity etc. can access the resin flow stream at this site. The optional sectors can be added or removed from service in accordance with the needs of the experiment and they can be customized to enhance sensor performance, e.g. installing optical windows for microscopy experiments. In this case, we have reserved an optional port sector for an ultrasonics sensor.

The alumina ceramic is positioned in a well that has been machined into the bottom half stainless piece and is held mechanically in place by clamping top and bottom halves together. No epoxy or other adhesive is needed. To change ceramic substrates, the alumina block is removed from its well using the lifting bolts on the bottom of the housing to push the block out of the well. It can be replaced with electroded alumina substrates with different electrode patterns that produce fringe electric fields closer and farther from the surface and directed parallel or perpendicular to the flow. Likewise, the ceramic with the slit in the top half of the sensor can be interchanged with pieces having different slit sizes.

A pattern of interdigitating electrodes is shown in Figure 4. Two sets of finger electrodes are interwoven to create the sensor. Each set of fingers is connected to a lead electrode. When an alternating voltage is applied between the electrodes, an electric field fringes between neighboring finger electrodes and extends not only through the alumina ceramic but also into the liquid media flowing above the surface. By measuring the value and phase of the resultant current and subtracting out the current through the alumina, the relative permittivity and dielectric loss of the liquid media can be determined. The electronics detecting circuitry and the software to operate the system is the same as has been used with the dielectric ring sensor and has been described in previous publications.[1,2]

The slit configuration accomplishes two objectives: first, it confines the flowing liquid to a thin ribbon for which a significant fraction of its cross section is intersected by the fringing electric field lines, and second, it is the geometry of a slit die rheometer so that with knowledge of the pressure drop across the length of the slit and the flow rate, the viscosity of the material can be determined. For this purpose, a pressure transducer is positioned upstream from the dielectric sensor and yields the value of the pressure drop along the axial length of the slit.

The optics sensor, shown in Figure 5, is situated upstream of the dielectric sensor in the stainless steel housing of the slit die. It consists of a bundle of seven 200 μm core optical fibers that are placed into a sleeved standard half-inch sensor bolt with a sapphire window at its end. It operates in the reflection mode, i.e. one of the fibers transmits light from the light source through a focusing lens, the sapphire window, the flowing liquid, reflects off the far stainless steel surface, and reverses its path through the material, sapphire window and lens. The reflected light is collected by the other six fibers and is transmitted to the photomultiplier detector. The intensity of the light source is monitored using a beamsplitter that sends a source sampling beam to another photomultiplier as shown in Figure 6. The ratio of the two light intensities is used to monitor the light transmission through the liquid.

Alternatively, the optical sensor can be used as a fluorescence temperature probe to monitor temperature of an extruded resin that has been doped with a temperature sensitive fluorescent dye. The technique employs the same optical equipment that is shown in Figure 6, excepting that bandpass filters, that are tuned to particular wavelengths of the fluorescence spectrum, are placed before the photomultiplier detectors. The measuring method has been described in detail in references 6 and 7.

Dielectric Measurements

When a material, for example a polymer melt, is subjected to an electrical field, bound charges are displaced and dipoles are oriented. Measurements made as a function of frequency of applied electric field and temperature yield basic information about molecular dynamics, ionic conductivity, thermally activated processes, and the role of microstructure on the development of interfacial polarization. The behavior is described by the complex relative permittivity ε* where

$$\varepsilon^* = \varepsilon' - i\varepsilon'' \qquad (1)$$

The real part of the relative permittivity ε' is associated with the polarization or capacitance of the material and the imaginary part ε", the dielectric loss, is associated with its conductance.

When measuring the dielectric properties of a polymer melt at elevated processing temperatures, ion conductivity becomes a prominent feature of the behavior. This is particularly true when fillers containing ionic species are compounded with a resin matrix. In some cases the ion conductivity is so large that it overrides molecular dipolar and microostructural relaxation processes. In general the conductivity σ can include a frequency independent component σ_{DC} associated with the drift of unbound charges and also a frequency dependent component σ_r related to dielectric relaxation,

$$\sigma = \sigma_{DC} + \sigma_r \qquad (2)$$

and

$$\varepsilon'' = \frac{\sigma_{DC}}{\omega \varepsilon_o} + \varepsilon_r'' \qquad (3)$$

where $\omega = 2\pi$ x frequency, $\varepsilon_0 = 8.854 \times 10^{-12}$ F/m and ε_r" is the frequency dependent part of the dielectric loss. Ionic conduction also contributes to the real part of the relative permittivity as electrode polarization or as interfacial polarization. Both of these phenomena usually occur at low frequency when ions can follow in phase with the applied electric field and accumulate at the electrode or, in a heterogeneous mixture, at the interface between components of different dielectric constant. The frequency dependence of interfacial polarization is known as Maxwell-Wagner relaxation. For composite materials, a distribution of permittivities and conductivities produces a distribution of relaxation times, effects that are the focus of our effort to monitor the dielectric properties of polymer composites.

Materials[a]

To demonstrate the operation of the slit die sensor, we present real-time monitoring data for compounding nylon 12 with montmorillonite clay. Nylon 12, Grilamide L16 natural, was obtained from EMS Chemie. The clay was an organically modified clay from Southern Clay Products, Clay 30B. The powdered clay was compounded with the polymer at 4 % mass fraction of clay in the polymer. Compounding was carried out using an 18 mm Haake Reocord model 9000 twin screw extruder.

Standard uncertainties for the measurements were 1 °C for temperature and 70 kPa (10 psi) for pressure. The standard uncertainty in relative permittivity is 0.01 and for conductivity it is 1×10^{-10} S/m. The relative standard uncertainty in the light transmission data is 0.15 %.

Results

Figure 7(a) shows real-time data for extrusion of nylon 12 (neat) and for nylon 12 compounded with 4 % Cloisite Clay 30B. Compounding was carried out at 195 °C. Relative permittivity and conductivity are plotted versus time for fifteen different frequencies ranging from 500 Hz to 100 kHz. At t = 400 s, the neat polymer entered the electrode region of the dielectric sensor and was extruded for approximately 1500 s, at which time resin pellets mixed with 4 % mass fraction of clay were added to the feeder. Permittivity and conductivity began to increase as the mixture filled the slit region. After significant transition time, the data reached a plateau value. The transition is associated with time it takes the clay/polymer mixture to completely fill the sensing region, particularly at the surface near the electrodes. At t = 4200 s, the neat resin was again introduced and relative permittivity values returned to their original values.

The difference in relative permittivity at low frequency (500 Hz) and high frequency (10^5 Hz) is called the dielectric dispersion. We see that the dispersion for the clay/polymer nanocomposite is considerably larger than that for the neat polymer. This is because the introduction of the clay particles to the resin introduces ionic species that contribute to conductivity and polarization over and above that which is present in the neat resin.

Figure 7 (b) and (c) show the corresponding pressure and optical signals as a function of time. Steady state conditions prevail after the transitions are complete. Calculation of resin apparent viscosity yielded values of 139.6 Pa.s and 169.4 Pa.s for the neat and filled polymer respectively. The relative uncertainty in the apparent viscosity values is 8 %.

Conclusions

The operation of a new dielectric slit die sensor has been demonstrated. It is a multi-functional device that delivers a package of data about the processed resin. A flexible design permits the addition of new sensors according to the demands of the experiment.

References

1. S. Perusich and M. McBrearty, Polym. Eng. Sci. **40**, 214 (2000).
2. A. J. Bur, S. C. Roth and M. McBrearty, Rev. Sci. Instr. 73, 2097 (2002).
3. A. J. Bur, S. C. Roth and M. McBrearty, Proc. SPE ANTEC 2002.
4. M. C. Zaretsky, P. Li, and J. R. Melcher, IEEE Trans. Elect. Insul. **24**, 1159 (1989).
5. A. J. Bur, S. C. Roth and M. McBrearty, Proc. SPE ANTEC 2003.
6. A. J. Bur, M. G. Vangel and S. C. Roth, Appl. Spect. **56**, 174 (2002).
7. A. J. Bur, M. G. Vangel and S. C. Roth, Polym. Eng. Sci. **41**, 1380 (2001).

Keywords: clay nanocomposites, dielectric sensor, process monitoring, optical sensor, slit die rheometer

[a] Identification of a commercial product is made only to facilitate experimental reproducibility and to describe adequately the experimental procedure. In no case does it imply endorsement by NIST or imply that it is necessarily the best product for the experiment.

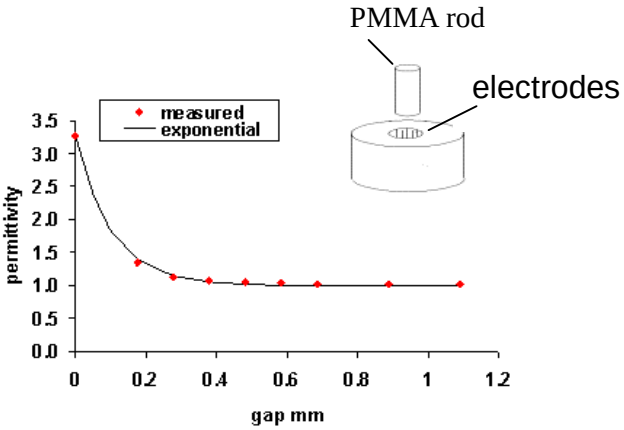

Figure 1. The decay of sensor sensitivity is shown for the 12.7 mm ID ceramic ring. Decay is exponential with characteristic length d/3 where d =0.33 mm, the electrode separation.

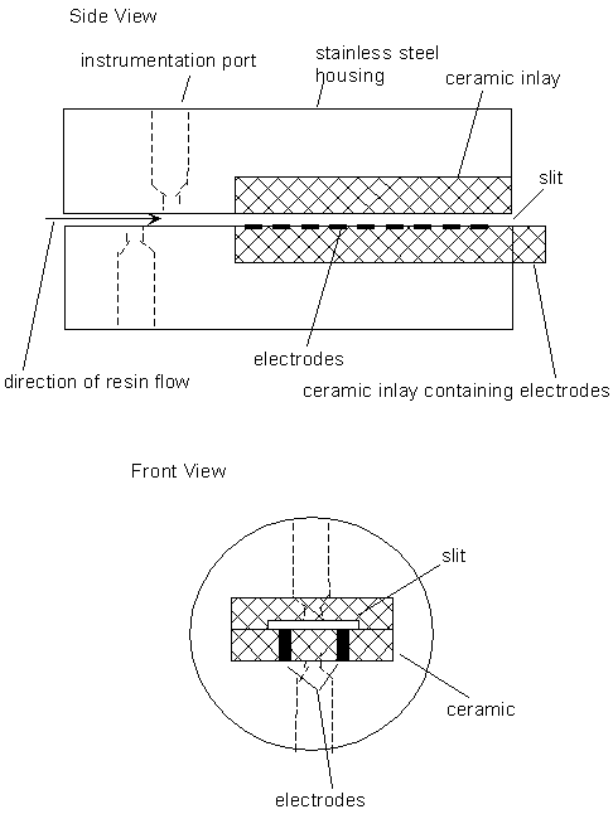

Figure 2. Side and front views of the dielectric slit die.

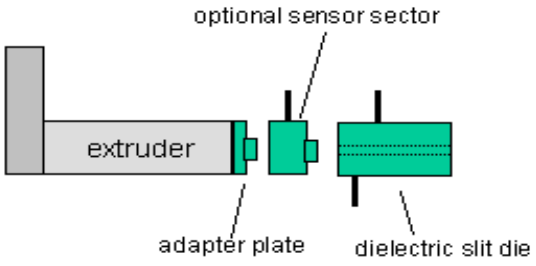

Figure 3. The position of the optional sensor port is shown.

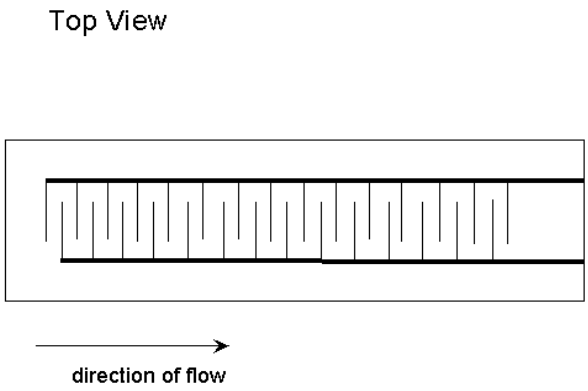

Figure 4. The pattern of interdigitating electrodes.

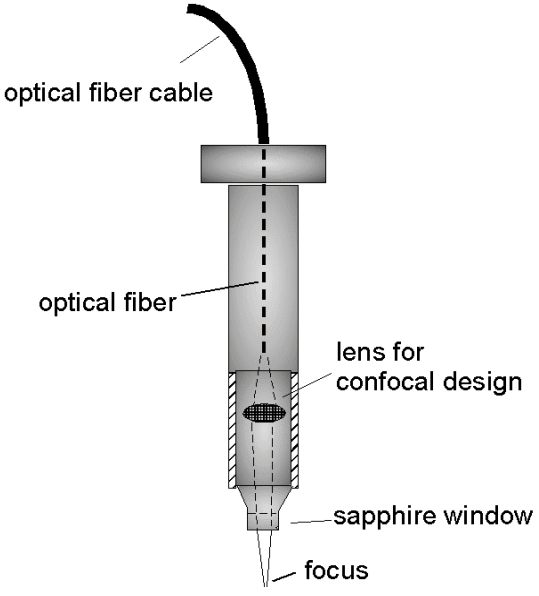

Figure 5. The standard half-inch bolt modified to receive optics.

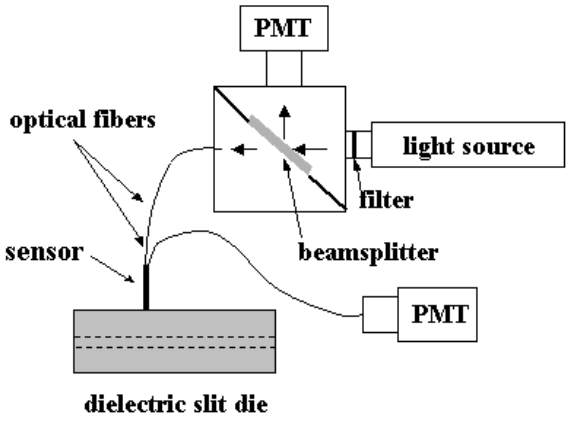

Figure 6 Optics light source and detection setup

.

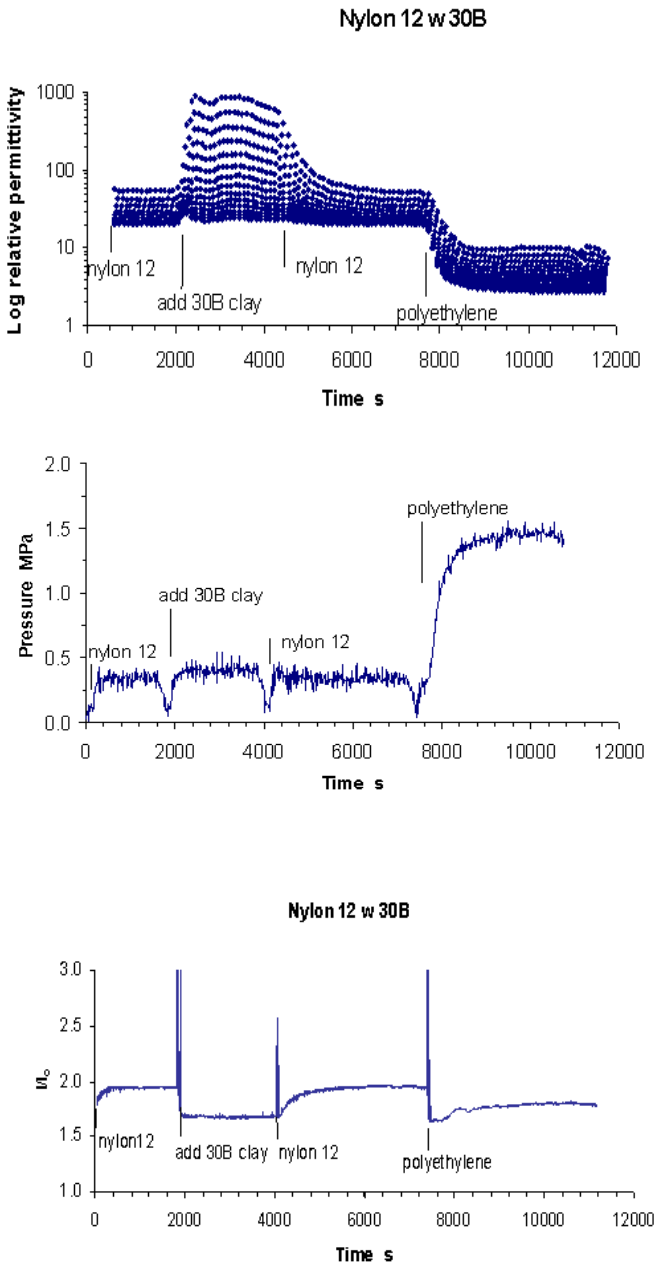

Figure 7. Permittivity, pressure and light transmission are plotted versus time for nylon 12 compounded with 30B clay.